washed with acetone and dried first in air and then in vacuum over phosphorus pentoxide. *Anal.* Found: S, 4.90; CH_3O, 3.08; ash (calcd. as K_2SO_4), 0.31. This disulfide was insoluble in hot aqueous ethanol and treatment with an excess of a mercaptan caused reduction to a soluble form. Addition of lead acetate to an aqueous solution of the potassium salt of N-mercaptomethyl-66 described above caused formation of a yellow precipitate.

Hydrolysis of N-Methoxymethyl-66 by Aqueous Acid.—The hydrolysis of the methoxymethyl group to CH_3OH, CH_2O and the unsubstituted amide group may be carried out in a controllable fashion and thus is an additional method for obtaining any given degree of methoxyl content.

Small strips of film (0.002" thick) of N-methoxymethyl-66 were suspended in a solution of 10 ml. of concentrated hydrochloric acid in one liter of water at 50° for various lengths of time. The strips were removed, washed thoroughly in water, soaked in aqueous ammonia, washed in water and finally dried in vacuum over phosphorus pentoxide.

Time in acid solution, minutes	CH_3O, %
0	7.13
1	6.61
2	5.41
3	4.57
4	2.77

Acid Cross-linking of N-Methoxymethyl-66.—A 20% solution of N-methoxymethyl-66 in methanol–water (80% methanol by weight) was prepared by stirring under reflux at 60°. To this was added maleic acid (1% based on the polymer) and the mixture stirred for thirty minutes to dissolve the acid. This solution was filtered under pressure, allowed to stand two hours at 60° to permit the air bubbles to rise out of the solution and was then cast into films on glass plates. The solvent was allowed to evaporate at room temperature for about twenty hours.

The pliable, transparent film prepared in this manner analyzed for 8.53% methoxyl. Baking this film (on the glass plate) for six hours at 60° gave a product of 6.94% methoxyl content; one hour at 100° gave a product of 6.31% methoxyl content. Both these baked films were found to be insoluble (although highly swollen) in hot 80% methanol, and they did not melt at any temperature but charred gradually about 295°. A film of the same N-methoxymethyl-66 prepared in a similar manner but without added acid melted at about 155° and was readily soluble in hot aqueous methanol even after baking for one hour at 100°.

Summary

The conversion of N-alkoxymethyl polyamides to alkylthiomethyl and mercaptomethyl polyamides by treatment with mercaptans or thiourea in the presence of strong acids has been described.

WILMINGTON, DELAWARE RECEIVED JULY 20, 1948

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF IOWA STATE COLLEGE]

Perylene, a By-product from Some 1-Naphthyl-metallic Compounds

BY HENRY GILMAN AND CECIL G. BRANNEN

Incidental to the preparation of some substituted silanes using 1-naphthyllithium, perylene was isolated from several different mixtures. Mr. L. Miller[1] isolated this hydrocarbon from the reaction between 1-naphthyllithium and silicon tetrachloride, while we have found it in some reactions of 1-naphthyllithium with ethyl silicate and hexachlorodisilane, as well as with silicon tetrachloride.

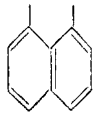
In order to determine if a silicon compound is essential for the formation of perylene, 1-naphthyllithium was made from 1-bromonaphthalene of the highest purity available, hydrolyzed, and the residue examined chromatographically. Pure perylene in a yield of 3% was isolated from the mixture.

There is no evidence in the literature that 1,8-dibromonaphthalene is formed during the bromination of naphthalene and even if traces are formed, it is improbable that perylene in the yield of 3% could have come from that source. To reduce further the possibility that perylene might have resulted from a dibromo isomer, 1-naphthyllithium was prepared from the halide obtained from a Sandmeyer reaction and the mixture examined as before. A 2.8% yield of perylene was found.

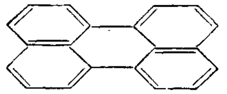
Among the mechanisms by which perylene might be produced in this reaction are: (1) the formation and disproportionation of free radicals, followed by coupling; and (2) a ring closure, by dehydrogenation, of an intermediary biaryl, 1,1'-binaphthyl. Free radical formation and disproportionation have been advanced by several investigators,[2] and in this case the mechanism may be as shown by the following set of reactions

$$1\text{-}C_{10}H_7Br + Li \longrightarrow 1\text{-}C_{10}H_7\text{-} + LiBr \quad (1)$$

$$2\ 1\text{-}C_{10}H_7\text{-} \longrightarrow 1,1'\text{-}C_{10}H_7\text{-}C_{10}H_7 \quad (2)$$

$2\ 1\text{-}C_{10}H_7\text{-} \longrightarrow$  $+ C_{10}H_8$ (3)

(I)

$2\ (I) \longrightarrow$  (4)

(II)

Some organometallic compounds are known to effect dehydrogenation[3] and such dehydrogenation

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[1] Unpublished studies, Iowa State College.

[2] (a) Gilman and St. John, THIS JOURNAL, **52**, 5017 (1930) (b) Kharasch and Fields, *ibid.*, **63**, 2316 (1941). (c) Wuis and Mulder, *Rec. trav. chim.*, **57**, 1385 (1938); Nauta and Mulder, *ibid.*, **58** 1062 (1939); Gomberg and Bachmann, THIS JOURNAL, **52**, 2455 (1930); Blicke and Powers, *ibid.*, **51**, 3378 (1929); Bachmann and Clarke, *ibid.*, **49**, 2089 (1927). For a discussion with leading references, see Gilman, "Organic Chemistry," 2nd ed., John Wiley and Sons, Inc., New York, N. Y., 1942, p. 540.

[3] Gilman and Bradley, THIS JOURNAL, **60**, 2333 (1938).

may lead to cyclization.[4] This may be represented by the equation

$$1,1'\text{-}C_{10}H_7\text{-}C_{10}H_7 \xrightarrow{1\text{-}C_{10}H_7Li} (II) \quad (5)$$

To check the validity of equation (5), pure 1,1'-binaphthyl was refluxed for several days with phenyllithium and the mixture was examined for perylene. The fluorescent material was separated from the bulk of binaphthyl by chromatographic purification and was shown to contain perylene by the characteristic absorption bands at 410 and 435 mμ. Similar results were obtained using *p*-dimethylaminophenyllithium instead of phenyllithium.

The formation of perylene is not peculiar to the lithium compound since traces were found in the products resulting from the hydrolysis of the Grignard reagent, 1-naphthylmagnesium bromide.

Acknowledgment.—The authors thank William Meikle for assistance.

Experimental

All identifications (other than those by absorption curves) were made by mixed m.p. The petroleum ether used as solvent had a b.p. of 90–115°. The perylene used was made by three methods: (1) from naphthalene[5a]; (2) from 1-bromonaphthalene[5b]; and (3) from β-dinaphthol.[5c] The m.p.'s and mixed m.p.'s of all combinations of the samples were 268–269° (cor.).

Perylene from the Hydrolysis of 1-Naphthyllithium.—One hundred grams (0.48 mole) of 1-bromonaphthalene ($n^{20}D$ 1.6578, sp. gr. $1.481^{20}/_{20}$) was added with stirring to 7.0 g. (1.0 g. atom) of lithium in 500 ml. of ether in an atmosphere of nitrogen, and refluxed one hour. The yield, as determined by acid titration,[6] was 96%. The ether solution was hydrolyzed with cracked ice, washed with water, steam distilled, and the resulting dark red solid residue, 11.8 g., dried *in vacuo* for forty-eight hours. After extraction in a Soxhlet for three days with petroleum ether, the 0.9 g. of insoluble residue, m.p. 190–260°, was discarded and the solution was diluted to 1 l. with pure solvent and examined chromatographically.

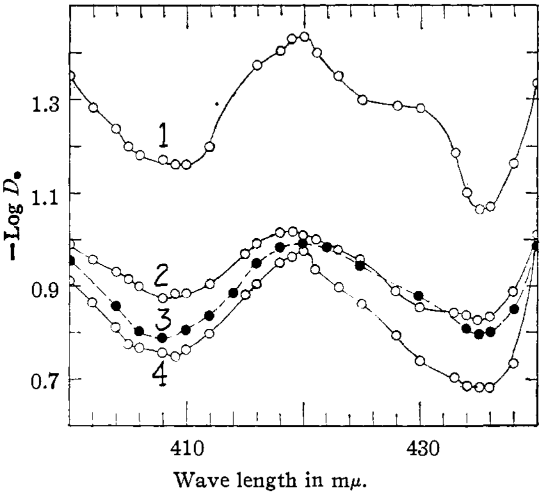

Fig. 1.—Ultraviolet absorption spectra in alcohol: (1) perylene (1.4 × 10^{-8} *M*); fluorescent material from (2) reaction of 1,1'-binaphthyl with *p*-dimethylaminophenyllithium, (3) prepn. of 1-naphthylmagnesium bromide, and (4) reaction of 1,1'-binaphthyl with phenyllithium. Measurements were made with a Beckman Spectrophotometer (Model DU).

A 40-ml. portion of the petroleum ether extract was diluted to 250 ml., poured through a 15 × 150 cm. column of alumina[7] and observed with ultraviolet light. After development with, first, 1 l. of pure solvent and, second, 1 l. of 10% benzene–petroleum ether, the solvents were separately evaporated, giving 79 mg. (3.1%) of crude perylene, m.p. 261–264°, from the first filtrate, and a few crystals (not weighed) of 1,1'-binaphthyl, m.p. 155–156°, from the benzene–petroleum ether filtrate. Several other zones developed in the column, but they were not investigated.

The same procedure was followed using 1-bromonaphthalene prepared[8] by a Sandmeyer reaction from purified 1-naphthylamine. The yield of perylene in this experiment was 2.8%.

Perylene (mixed m.p.) was also obtained by the action of lithium metal on 1,1'-binaphthyl.

1,1'-Binaphthyl and Phenyllithium.—Ten grams of 1,1'-binaphthyl,[9] m.p. 155–156°, and 0.3 mole of phenyllithium in ether were refluxed under nitrogen for fifty-two hours and then poured onto cracked ice. The ether layer was washed with water and the solvent removed. The residue was dissolved in dry petroleum ether and the resulting yellow solution poured through an alumina column. The blue fluorescent zone was cut off, eluted, dried overnight at 130° and the adsorbed material was dissolved in 200 ml. of 95% ethanol. The absorption curve of the solution is shown in Fig. 1.

The authors are grateful to Dr. Robert R. Sealock for assistance.

1,1'-Binaphthyl and *p*-Dimethylaminophenyllithium.—Five grams (0.02 mole) of 1,1'-binaphthyl, m.p. 156°, added to 0.2 mole of *p*-dimethylaminophenyllithium in 250 ml. of ether, was refluxed for fourteen hours and then poured onto cracked ice. The ether solution was thoroughly washed with hydrochloric acid and water, dried with sodium sulfate, and concentrated. The residue was dissolved in 1 l. of petroleum ether and chromatographed. After two passes through a 15 × 150 cm. alumina column, 4.8 g. (96%) of the 1,1'-binaphthyl was recovered from the filtrate, while a bright blue fluorescent zone developed on the column. The blue zone was eluted with ether, the solvent removed, and the residue was dried and dissolved in 200 ml. of 95% ethanol. The absorption spectrum is shown in Fig. 1.

Perylene from the Hydrolysis of 1-Naphthylmagnesium Bromide.—Forty-one and four-tenths grams (0.2 mole) of 1-bromonaphthalene was added to 5.0 g. (0.21 g. atom) of magnesium in ether under the usual conditions to give a 96% yield of the Grignard reagent. The ether solution was carbonated by pouring upon crushed Dry Ice, extracted with 20% sodium hydroxide, washed with water and the solvent removed. The residue was dissolved in petroleum ether and chromatographed. The filtrate contained 2.1 g. (0.008 mole) of 1,1'-binaphthyl, m.p. 156°, while the column contained a blue fluorescent zone. The blue zone was cut off and eluted with ether, the solvent removed, and the residue dried. Substantial evidence that the residue contained perylene was obtained by comparison of the ultraviolet spectrum of the ethanol solution of this residue with that of an authentic sample of perylene in ethanol; see Fig. 1.

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[4] Fuchs and Grosz, *Ber.*, **63**, 1009 (1930).

[5] (a) Scholl, Seer and Weitzenbock, *Ber.*, **43**, 2203 (1910); (b) Weitzenbock and Seer, *Ber.*, **46**, 1996 (1913); (c) Brass and Tengler, *ibid.*, **64B**, 1648 (1931).

[6] Gilman, Wilkinson, Fishel and Meyers, THIS JOURNAL, **45**, 150 (1923).

[7] Fisher Scientific Co., 80–200 mesh.

[8] Prepared by Mr. R. Brennan of this Laboratory.

[9] Prepared by the method of Krizewsky and Turner, *J. Chem. Soc.*, **115**, 559 (1919), from the Grignard reagent and cupric chloride and purified chromatographically on alumina from petroleum ether.

1-Naphthyllithium and Silicon Compounds.—Perylene was isolated from several mixtures resulting from the separate treatment of silicon tetrachloride, ethyl silicate and hexachlorodisilane with 1-naphthyllithium. In all cases the 1-napthyllithium was made in the conventional manner from the bromide and lithium.

A typical run is described. 1-Naphthyllithium (0.26 mole) in 400 ml. of ether was added to 17.9 g. (0.086 mole) of ethyl silicate and refluxed overnight. The ether was replaced with benzene, the solution filtered and the filtrate was concentrated to about 50 ml. and allowed to crystallize. The yellow solid, m.p. 190–210°, after two crystallizations from benzene melted at 268–269° and showed no depression of m.p. when mixed with perylene. The yield from this run was 2.1%.

Similar runs using silicon tetrachloride gave yields of perylene from 1.2 to 2.6%, and with hexachlorodisilane, 2.2 and 2.4%. The evidence is, therefore, that the silicon compounds play no significant part in the formation of perylene.

Summary

The hydrocarbon, perylene, has been isolated from several reaction mixtures involving 1-naphthyllithium and 1-naphthylmagnesium bromide. The formation of perylene from the 1-naphthylmetallic compounds may be due in part to a free radical mechanism and also to a cyclodehydrogenation of 1,1′-binaphthyl by means of organolithium compounds. Experiments are presented in support of this latter mechanism.

AMES, IOWA RECEIVED AUGUST 23, 1948

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF IOWA STATE COLLEGE]

Characterization of Sulfonic, Sulfinic, Phosphonic and Some Other Acids as Thallous Salts

BY HENRY GILMAN AND R. K. ABBOTT, JR.[1]

It has been suggested[2] that thallous sulfonates may be reagents of choice in the characterization of some sulfonic acids. Several advantages of the thallous salts as derivatives of the sulfonic acids were detailed in a previous contribution.[2] The present report extends the scope of the reaction to other types of acids, and also further defines certain limitations in the usefulness of the reaction.

Although the thallous arylsulfonates meet the requirements for good derivatives, the thallous alkylsulfonates appear to be less satisfactory derivatives.

The arylsulfinic acids appear to be conveniently characterized as thallous salts.

The aromatic thiols give excellent derivatives, but the aliphatic thiols give salts having insufficiently sharp melting points. Moreover, the thallous mercaptides are evidently unstable, decomposing on standing in the dark in tightly stoppered vials. However, the quantitative formation of the highly colored thallous mercaptides suggests their use as extremely sensitive qualitative tests for the detection of mercaptans.

Both arylphosphonic acids and arylphosphinic acids are readily characterized by this method. Either the mono- or the di-thallous salts of the phosphonic acids provide derivatives with good melting points.

Nitromethane and nitroethane readily form monothallous salts, but only the latter has a definite decomposition point.

2,4,6-Trinitrobenzoic acid gives a crystalline monothallous salt, melting with decomposition at 160–163°, which decarboxylates smoothly in boiling pyridine solution giving 1,3,5-trinitrobenzene and thallous oxalate. Thallous 2,4,6-trinitrobenzoate reacts further with a second equivalent of thallous hydroxide giving a blood-red complex of uncertain composition. 1,3,5-Trinitrobenzene was found likewise to react with one, two and three equivalents of thallous hydroxide giving complexes of rather indefinite composition which explode on heating.

Thallium trichloride reacts with sodium *p*-toluenesulfinate and with *p*-toluenesulfinic acid to give thallium dichloride *p*-toluenesulfinate.

$$p\text{-CH}_3\text{C}_6\text{H}_4\text{SO}_2\text{Na} + \text{TlCl}_3 \longrightarrow p\text{-CH}_3\text{C}_6\text{H}_4\text{SO}_2\text{TlCl}_2 + \text{NaCl}$$

However, the interesting observation was made that this compound did not eliminate sulfur dioxide with the formation of a carbon–metal linkage, as has been observed with some related mercury compounds.[3]

Experimental

Two general procedures have been mentioned[2] for the preparation of thallous sulfonates. These procedures were used for the thallous salts described in Table I. The most important point in their preparation is the recrystallization solvent. In most cases it was desirable to evaporate the solution of salt almost to dryness and then recrystallize the salt from ethanol–water mixtures since most of them are very soluble in water and much less soluble in ethanol.

Thallium Dichloride *p*-Toluenesulfinate.—On mixing 0.1 mole each of sodium *p*-toluenesulfinate and thallium trichloride dissolved in a minimum of water, there was an immediate precipitate accompanied by an odor of *p*-toluenesulfonyl chloride. The precipitate was filtered, washed, and dried giving 36 g. (84%) of the salt, which melted at 203–205° (dec.).

Anal. Calcd. for $\text{C}_7\text{H}_7\text{O}_2\text{Cl}_2\text{STl}$: Tl, 47.4. Found: Tl, 47.6.

2,4,6-Trinitrobenzoic Acid and Two Equivalents of Thallous Hydroxide.—In order to determine whether the red precipitate transitorily encountered in the preparation

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[1] Present address: General Electric, S. A., Caixa Postal 109, Rio de Janeiro, Brazil.

[2] Gilman and Abbott, THIS JOURNAL, 65, 123 (1943).

[3] Peters, *Ber.*, 38, 2567 (1905); Kharasch, THIS JOURNAL, 43, 610 (1921); Loudon, *J. Chem. Soc.*, 823 (1933).